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Synthesis of deuterobutadiene-butadiene AB_2 and AB_3 miktoarm star copolymers

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Abstract

The synthesis of well-defined, monodisperse AB_2 and AB_3 miktoarm star copolymers, in which A is polydeuterobutadiene and B is polybutadiene, is described. The synthetic procedure involved reacting living polydeuterobutadiene with a large excess of either methyltrichlorosilane or tetrachlorosilane to yield a 'one-arm star'. SEC traces of this 'one-arm star' are indistinguishable from that of the uncoupled polydeuterobutadiene indicating no further coupling to form multi-arm stars occurs. Unreacted chlorosilane was removed by distillation and the introduction of an excess of living polybutadiene generates the star. The star polymer was isolated from the precursor polybutadiene by fractionation.

Introduction

The use of anionic polymerisation techniques and chlorosilane coupling agents in the synthesis of star-branched polymers, which are well defined in terms of the molecular weight of the individual arms and the number of arms is well documented (1-10). These novel compounds, which, as well as being of interest in their own right, constitute excellent models for branched polymers and the crosslink points of networks, have been studied extensively and many of the results and conclusions have been reviewed recently (11). Virtually all of the investigations have been concerned with the global properties of the star, the configurational properties of the individual arms being deduced from these properties or explicitly presumed.

More recently the design and synthesis of novel, well-defined star-branched polymers having chemically different arms has received much attention. Hadjichristidis and co-workers have produced a number of stars of this type including an ABC miktoarm star terpolymer (12) in which A is polyisoprene, B polystyrene and C polybutadiene, an ABCD miktoarm star quaterpolymer (13), in which A, B and C are as above and D is poly(4-methylstyrene) and an A_8B_8 miktoarm star copolymer (14) where A is polystyrene and B polyisoprene. Other work includes the preparation of styrene-isoprene A_2B_2 (15, 16), A_2B and A_3B (17, 18) stars.

In the present work we have adopted the general approach of Hadjichristidis et al to synthesise AB_2 and AB_3 miktoarm star copolymers where A is polydeuterobutadiene and B is polybutadiene. Selectively labelled star-branched polymers of this type open up new possibilities for the investigation of some of the physical dimensions of a single arm within the star. Such investigations have not been possible to date. Small angle neutron scattering experiments have been carried out and the results will be discussed in a future publication.

Experimental

Butadiene was purified by passing the monomer successively through columns of Carbosorb (Aldrich), to remove any inhibitor, and molecular sieve, to dry the monomer. Deuterobutadiene was prepared by reductive dechlorination of hexachlorobutadiene using zinc dust, sodium iodide and cupric chloride in 1,4-dioxane according to the procedure of Craig and Fowler (19). Benzene was washed with concentrated sulphuric acid, dried with calcium hydride and degassed by a number of freeze thaw cycles. *Sec*-butyllithium, tetrachlorosilane and methyltrichlorosilane (all Aldrich) were used as purchased.

The miktoarm stars were prepared in a single apparatus containing two separate reaction vessels. The apparatus was evacuated and washed with a solution of living polystyryllithium (PSLi) prior to use, to remove any residual water (or other protic impurities) from the inside surfaces. Solvent was then distilled from the reservoir of PSLi and the surfaces rinsed clean of any residual PSLi, the solvent (and residues) being decanted back into the PSLi reservoir. This rinsing process was repeated until the solvent being returned to the reservoir of PSLi was water white, i.e. free from any of the bright orange PSLi. All polymerisations were carried out using standard high vacuum techniques with benzene as the solvent and *sec*-butyllithium as the initiator, the latter being injected through a septum. The miktoarm stars were isolated from excess precursor polybutadiene by fractionation using toluene as solvent and methanol as non-solvent. Molecular weights and polydispersities of the isolated, dried polymers were obtained by SEC using THF as the solvent and both differential refractometer and viscometer detection. The data were analysed using Viscotek Unical GPC-viscometry software version 4.06. Absolute values of the weight average molecular weights were obtained using a light scattering detector attached to the SEC.

Results and Discussion

Synthesis of AB_2 and AB_3 miktoarm star polymers depends on the reaction between the living polymer and a large excess of a chlorosilane linking agent, for example methyl trichlorosilane, resulting in the addition of no more than one polymer arm per silane molecule and the fact that the excess chlorosilane can be removed from the reaction vessel by vacuum transfer.

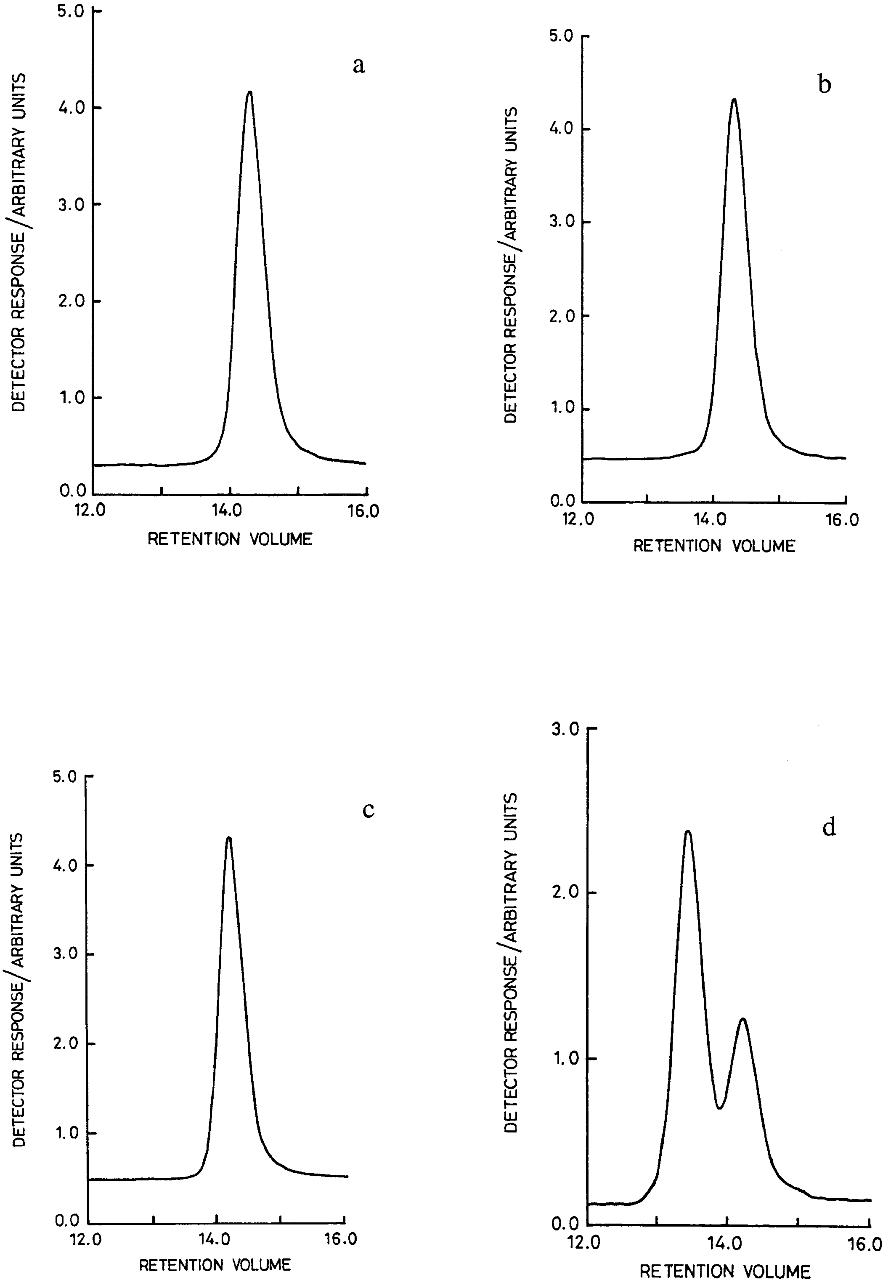
The reaction scheme used in the synthesis of the AB_2 miktoarm star polymer is shown below:

$$\text{Butadiene-d}_6 + s\text{-BuLi} \longrightarrow \text{Polydeuterobutadienyllithium (PdBdLi)}$$

$$\text{Butadiene} + s\text{-BuLi} \longrightarrow \text{Polybutadienyllithium (PBdLi)}$$

$$\text{PdBdLi} + \text{excess Si(CH}_3\text{)Cl}_3 \longrightarrow \underset{\text{‘one-arm star’}}{\text{PdBd-Si(CH}_3\text{)Cl}_2} + \text{LiCl} + \text{Si(CH}_3\text{)Cl}_3 \uparrow$$

$$\text{PdBd-Si(CH}_3\text{)Cl}_2 + \text{excess PBdLi} \longrightarrow \underset{\text{AB}_2\text{ miktoarm star polymer}}{\text{(PdBd)(PBd)}_2\text{SiCH}_3} + \text{LiCl}$$


a
DETECTOR RESPONSE/ARBITRARY UNITS
5.0
4.0
3.0
2.0
1.0
0.0
12.0
14.0
16.0
RETENTION VOLUME
b
DETECTOR RESPONSE/ARBITRARY UNITS
5.0
4.0
3.0
2.0
1.0
0.0
12.0
14.0
16.0
RETENTION VOLUME
c
DETECTOR RESPONSE/ARBITRARY UNITS
5.0
4.0
3.0
2.0
1.0
0.0
12.0
14.0
16.0
RETENTION VOLUME
d
DETECTOR RESPONSE/ARBITRARY UNITS
3.0
2.0
1.0
0.0
12.0
14.0
16.0
RETENTION VOLUME

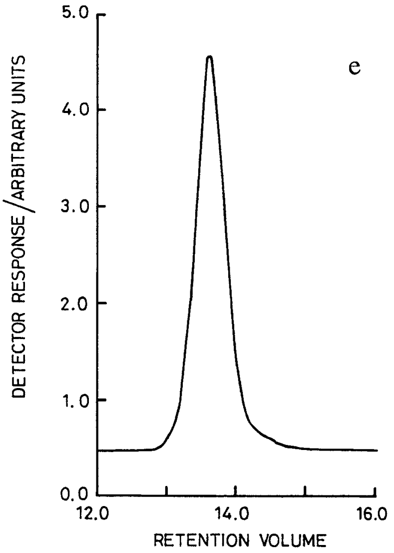


Figure 1. a) SEC chromatogram of polydeuterobutadiene precursor, PdBd; b) SEC chromatogram of 'one-arm star', PdBd-Si(CH_3)Cl_2; c) SEC chromatogram of polybutadiene precursor, PBd; d) SEC chromatogram of unfractionated AB_2 miktoarm star polymer; e) SEC chromatogram of fractionated AB_2 miktoarm star polymer.

Deuterobutadiene polymerisation was carried out in benzene initiated by *sec*-butyllithium, the target molecular weight for both PdBd and PBd was 30 000 gmol^{-1}. To obtain complete monomer conversion, a conservative approach was adopted, and the polymerisation allowed to run overnight, with stirring, at 313K after which a sample of the polymer was removed for molecular weight determination. A large excess (mole ratio Si:Li of 25: 1) of the linking agent methyl trichlorosilane was then added from a gas-tight syringe via the septum to the living polymer solution and the mixture stirred for a further 2 hours before a second sample was taken for molecular weight determination. The SEC trace for the 'one-arm star' (PdBd-Si(CH_3)Cl_2) is indistinguishable from that of the PdBd precursor see figures 1a and 1b. It is vitally important that the addition of the silane is made to the polymer solution (not vice versa) and that the silane is added undiluted (20). If either the polymer was added to the silane (diluted or undiluted) or a solution of the silane was added to the polymer solution then the reaction did not yield exclusively 'one-arm star'. In such cases a mixture of the desired product and undesirable higher molecular products (as a result of multiple polymer coupling to give some two-arm and maybe some three-arm star) is obtained, as shown by the SEC trace, see figure 2. The key to avoiding multiple coupling is a high ratio of silane to polymer. Consequently, it is presumed that at the point of addition of the neat silane to a polymer solution there is, locally, a very high ratio of silane to polymer. Addition of the silane as a solution reduces this local high ratio and results in some multiple coupling. Addition of polymer solution to silane, whilst appearing to be the logical approach, also results in multiple coupling.

Excess methyl trichlorosilane and solvent were removed from the reaction vessel by vacuum transfer. Dry, clean benzene was distilled into the reactor to redissolve the polymer and then removed by vacuum transfer. This procedure was repeated two more times to ensure complete removal of the excess chlorosilane. The $PdBdSi(CH_3)Cl_2$ was redissolved in benzene and the solution of pre-prepared PBdLi added, in sufficient quantity to give a 25% excess of PBdLi with respect to remaining C1 on the $PdBdSi(CH_3)Cl_2$. The mixture was stirred for 48 hours at 313-323K. Excess living PBd was terminated with nitrogen sparged methanol and the crude product collected by precipitation into methanol. The AB_2 miktoarm star polymer was isolated from the excess precursor PBd by fractionation with toluene as the solvent and methanol the non-solvent. SEC traces of the PBd precursor, the crude and the isolated miktoarm star polymer are shown in figures 1c, 1d and 1e and the molecular weights for the precursor polymers PdBd and PBd and the miktoarm star polymer are shown in Table 1.

Polymer	$\overline{M}_w$ **(g mol^{-1})**	$\overline{M}_n$ **(g mol^{-1})**	$\overline{M}_w/\overline{M}_n$	**Light Scattering** $\overline{M}_w$ **(g mol^{-1})**
PdBd	33 200	32 400	1.02	-
PBd	31 700	31 100	1.02	-
Miktoarm Star	90 500	88 200	1.03	87 000

Table 1.
Molecular weights and polydispersities of AB_2 Miktoarm Star and precursor polymers.

Molecular weights are very close to the target molecular weights and the polydispersities ($\overline{M}_w/\overline{M}_n$) are low, indicating narrow molecular weight distributions. The molecular weight of the miktoarm star is in good agreement with the value predicted from the molecular weights of the precursor arms, $\overline{M}_w$ of 90,500 cf predicted value for $\overline{M}_w$ of 96,600. This discrepancy is within acceptable margins of error for SEC.

The synthetic procedure for the preparation of an AB_3 miktoarm star polymer is essentially the same as that described above for the AB_2 miktoarm star polymer, except the linking agent methyltrichlorosilane is replaced with tetrachlorosilane. Molecular weights of the precursor polymers PdBd and PBd and the miktoarm star polymer are given in Table 2.

Polymer	$\overline{M}_w$ **(g mol^{-1})**	$\overline{M}_n$ **(g mol^{-1})**	$\overline{M}_w/\overline{M}_n$	**Light Scattering** $\overline{M}_w$ **(g mol^{-1})**
PdBd	30 100	29 400	1.02	-
PBd	31 200	30 800	1.04	-
Miktoarm Star	117 500	113 300	1.04	117 800

Table 2.
Molecular weights and polydispersities of AB_3 Miktoarm Star and precursor polymers.

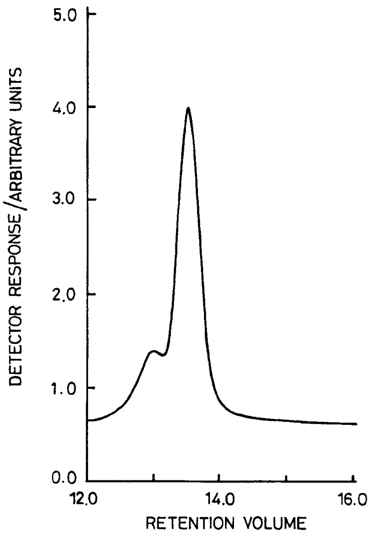


Figure 2. SEC chromatogram showing the multiple coupling obtained as a result of adding polymer solution to silane solution rather than pure silane to polymer solution.

As with the AB_2 miktoarm star polymer and its precursor polymers, the molecular weights are very close to the target molecular weights (30,000 $gmol^{-1}$) and the polydispersities ($\overline{M}_w/\overline{M}_n$) are low, indicating narrow molecular weight distributions. The molecular weight of the miktoarm star is once again in good agreement with the value predicted from the molecular weights of the precursor arms, $\overline{M}_w$ of 117,500 c.f. predicted value for $\overline{M}_w$ of 123,700. This discrepancy is within the acceptable margins of error for SEC. Small angle neutron scattering data on these miktoarm star copolymers have been obtained and will be reported in the future.

Conclusions

A synthetic method has been devised to prepare AB_2 and AB_3 miktoarm star copolymers in which one arm (A) of the star is the deuterium labelled isomer of the other arms (B). The synthetic procedure involves a combination of anionic polymerisation techniques and chlorosilane chemistry. SEC data demonstrates unequivocally that star polymers with one labelled arm have been obtained (following fractionation to remove excess hydrogenous arm polymer). These methods have been modified to enable the preparation of AB_n miktoarm stars with up to twelve arms. This will be reported in later papers.

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